Anion Inclusion by a Calix[4]arene Complex: a Contrast Between Tetranuclear Gold(I) and Copper(I) Complexes

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A tetradentate ligand, L, derived from a bowl-shaped calix[4]resorcinarene by incorporation of four phosphonite donors, has been used in the synthesis of several tetragold(I) and tetracopper(I) complexes, such as [L(AuCl)$_4$] and [pyH]$^+$[LCu$_4$(μ-Cl)$_4$(μ_3-Cl)]$^-$; the halide inclusion found for the copper complexes is unique in calixarene chemistry.
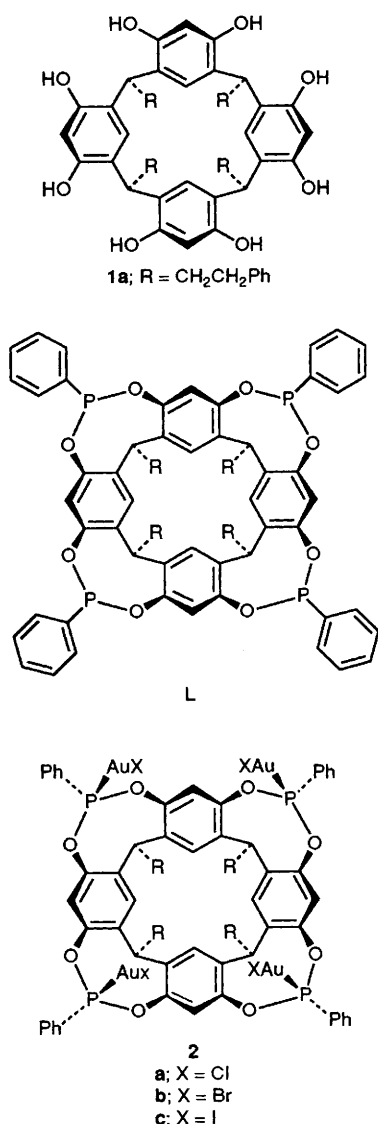
Calixarenes are bowl-shaped molecules that have a remarkable ability to contain either neutral or cationic guests.[1–3] However, owing to the poor electrophility of calixarenes, there is little anion inclusion chemistry and no halide inclusion.[4] This paper reports the derivatization of the upper rim of calixarenes to give phosphorus donors whose metal complexes provide a suitable environment for anion inclusion. Most known metal derivatives of calixarenes are with oxophilic metal ions, which cannot easily be used for anion inclusion.[2,3]

Reaction of the calix[4]resorcinarene, **1a**, R = CH$_2$CH$_2$Ph,[1] with phenyldichlorophosphine, with pyridine as base, gave the new phosphorus(III) derivative L. There are six possible isomeric forms of compound L, with different combinations of orientations of the phenyl and lone-pair substituents on phosphorus, either outwards or inwards with respect to the middle of the bowl. Molecular mechanics calculations indicated that the isomer with all phenyl groups directed outwards and lone pairs directed inwards would be preferred and this stereochemistry is consistent with the observation of a single ^{31}P NMR resonance for L.†

Reaction of ligand L with [AuCl(SMe$_2$)] occurred with displacement of SMe$_2$ to give [L(AuCl)$_4$], **2a**, X = Cl. The complexes **2b**, X = Br and **2c**, X = I, were then prepared
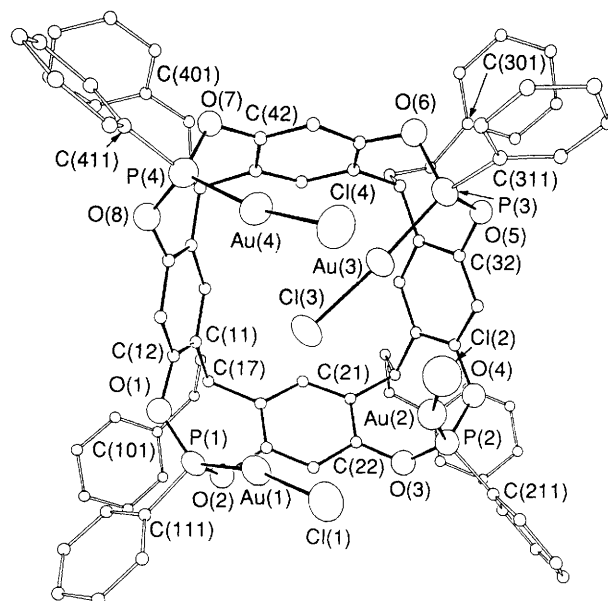
1a; R = CH₂CH₂Ph

L

2

a; X = Cl
b; X = Br
c; X = I

Fig. 1. A view of the structure of complex 2a. The Au–Cl and Au–P distances range from 2.270(6)–2.297(6) Å and 2.191(6)–2.223(6) Å respectively. The P–Au–Cl units are all somewhat distorted from linearity [range of angles P–Au–Cl 164.2(2)–167.7(2)°], apparently as a result of repulsive interactions between different AuCl units. For example, the shortest non-bonded Au···Cl distance is Au(3)···Cl(2) 3.359(8) Å and the repulsive interaction on Cl(2) leads to the angle P(2)–Au(2)–Cl(2) 164.2(2)°.

by reaction of 2a with the corresponding sodium halide. In each case, the ³¹P NMR spectra of the gold complexes 2 contained only one resonance, consistent with the expected stereochemistry with all phenyl substituents directed outwards and all AuCl substituents inwards, and this was confirmed by an X-ray structure determination on complex 2a·0.5CH₂Cl₂·2.5MeCN·H₂O.‡§ The structure of 2a is shown in Fig. 1. Three of the roughly linear AuCl units form a 'picket fence' around the upper rim of the bowl but the fourth AuCl unit [Au(3)Cl(3) in Fig. 1] is folded into the centre of the bowl and so occupies the cavity normally available to a guest molecule. As a result, the solvent molecules occupy regions of space between and not inside the potential host molecules. Nevertheless, since all PAuCl units are equivalent on the NMR time scale even at −80 °C, it is clear that the Au(3)Cl(3) unit can easily move to the periphery of the bowl and hence that small guest molecules could be admitted. The ligand holds the gold atoms apart and prevents any Au···Au bonding.[5]

Treatment of ligand L with [(CuCCPh)ₙ] in the presence of pyridinium chloride gave [C₅H₅NH] [LCu₄(μ-Cl)₄(μ₃-Cl)], 3a, in high yield (76%) with release of HCCPh which can be recovered quantitatively. Ligand L failed to react with (CuCCPh)ₙ in the absence of pyridinium chloride. The structure of 3a was determined by X-ray structure determination and the anion is shown in Fig. 2.¶‖ The main structural features are summarized as follows: (i) there is a Cu₄(μ-Cl)₄ unit arranged in a crown shape around the bowl rim, and so closing the bowl, in which the Cu–Cl bond distances are in the range 2.306(6)–2.410(5) Å; (ii) a Cl⁻ ion is trapped inside the bowl and is more weakly bound to three of the copper atoms with Cu–Cl distances in the range 2.467(5)–2.548(6) Å; (iii) as a result, the atoms Cu(1)–Cu(3) have irregular tetrahedral geometries with bond angles Cl–Cu–Cl in the range 95.1(2)–109.7(2)° while Cu(4) has trigonal planar geometry. This crown structure is unprecedented in tetranuclear copper(I) halide derivatives, for which cubane or ladder structures are typical.[6]

The bromide and iodide derivatives of 3 (3b, X = Br; 3c, X = I) can be obtained either from 3a by halide exchange using LiBr and NaI respectively or by direct reaction of L with (CuCCPh)ₙ in the presence of C₅H₅N·HCl and LiBr or NaI. The occluded μ₃-Cl as well as the more exposed μ₂-Cl ligands

expected. This indicates that the anions **3** are fluxional, with the trapped μ_3-Cl ligand migrating rapidly between the four copper atoms to give effective fourfold symmetry. This type of inclusion compound appears to be unique for the calixarenes and is made possible by the presence of the electrophilic copper(i) centres.

The difference in the preferred stereochemistries of gold(i) and copper(i) clearly has a profound effect on the ability of the bowl complexes to occlude a halide ion. The gold complex does not bind halide ions strongly whereas the copper complex does. Clearly, by modifying the metal substituents, there is the potential to tune the halide binding ability.
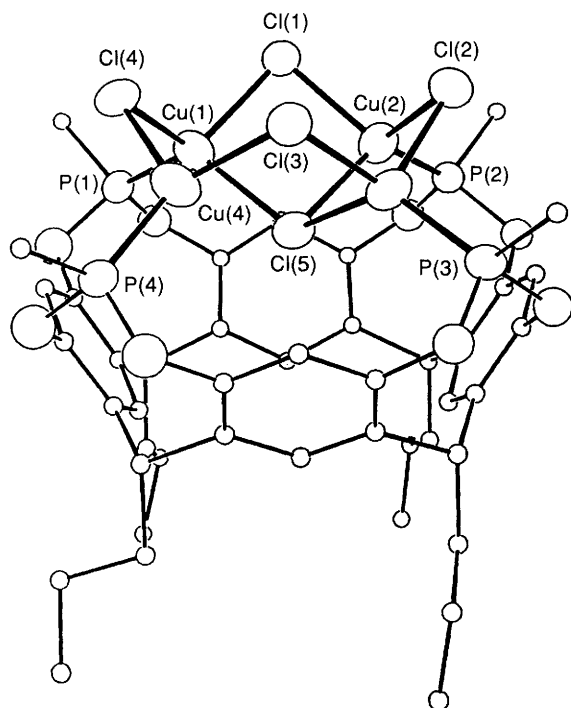
Fig. 2. A side view of the molecular structure of **3a**. The phenyl rings (both PPh and CH_2CH_2Ph) have been omitted for clarity. The guest chloride ion is Cl(5).

of **3a** are readily replaced by bromide or iodide. The ^{31}P NMR spectra of complexes **3** in CH_2Cl_2 solution contain only one resonance either at room temperature or at −90 °C whereas, in the solid-state structure, three such resonances would be

References

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